



## 20. Inclusion Polymerization of Vinyl chloride Monomer in Deoxycholic Acid Host via $\gamma$ -ray irradiation

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### Abstract

Inclusion polymerization of vinyl chloride monomer (VCM) was studied in the system of 3 $\alpha$ , 12 $\alpha$ -dihydroxy-5 $\beta$ -cholan-24-oic acid (deoxycholic acid, DCA). DCA-VCM inclusion compound system was originally prepared by guest intercalation technique in DCA guest free crystal. The inclusion polymerization of DCA-VCM by  $\gamma$ -irradiation at total dose 2 Mrad, gives a syndiotactic rich polyvinyl chloride (PVC) as can be confirmed by FT-IR and FT-NMR.

**Keywords:** Inclusion Polymerization, Deoxycholic Acid, Vinyl Chloride Monomer, Polyvinyl chloride,  $\gamma$ -ray Irradiation

### Introduction

The stereochemically controlled structure of polymer is known to be achieved in various systems, especially by using catalysts, such as Ziegler-Natta, and metallocene. Alternatively, inclusion polymerization is a unique technique to prepare controlled structure polymer by polymerization in microspace at a molecular level of inclusion compound, as seen in traditional system conducted by urea, thiourea<sup>1</sup>, cyclodextrin, dialkyl muconates<sup>2</sup>, etc., via photoinitiated polymerization.

Miyata *et al.* reported that steroid compound, such as, deoxycholic acid (3 $\alpha$ , 12 $\alpha$ -dihydroxy-5 $\beta$ -cholan-24-oic acid, DCA), apocholic acid (3 $\alpha$ , 12 $\alpha$ -dihydroxy-5 $\beta$ -

chol-(8)14-en-24-oic acid, ACA)<sup>3</sup>, and cholic acid (3a, 7a,12a-dihydroxy-5b-cholan-24-oic acid, CA), can provide suitable cavity size, shape, polarity, and chirality for vinyl monomer acrylic or cyclic conjugated diene and diacetylene monomer<sup>4</sup>. Interestingly, there is no report about inclusion polymerization of vinylchloride monomer until 1975 when Yoshii *et al.* studied the polymerization of vinylchloride monomer in urea to obtain syndiotactic poly(vinylchloride)<sup>5</sup>.

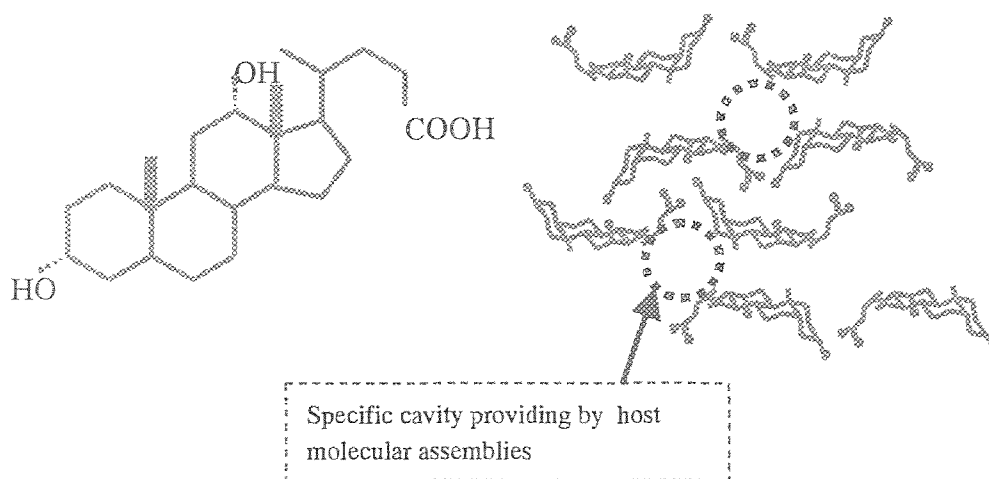


Figure 1. DCA structure and its molecular assembly with specific cavity

The present work was focused on the inclusion compound system between vinylchloride monomer and DCA, which is obtained from guest free structure of DCA host, combining with the intercalation technique. This work was also extended to the study of photopolymerization conditions by  $\gamma$ -ray and the characterization to clarify the stereoregularity of the obtained PVC.

## Materials

DCA (AR grade) was purchased from Nacalai Chemical, Japan and used without purification. Dioxane (AR grade) was purchased from Lab Scan (Thailand). Ethylacetate, o-xylene and p-xylene were purchased from Ajax Chemical and used without purification. Methyl alcohol anhydrous (AR grade) was purchased from

Mallinckrodt. Vinylchloride monomer was supplied by Thai Plastic and Chemicals Public Co., Ltd.

#### *Preparation of Inclusion Compound*

DCA was recrystallized by each solvent to obtain the transparent needle-like crystal. The guest free DCA was obtained by heating the DCA-solvent adducts at 140 °C for 12 hours under reduced pressure around 1020 mbar to remove solvent guest molecules. DCA-VCM was prepared as follows; one gram of guest free DCA and vinylchloride monomer that was trapped by using vacuum distillation at very low temperature (-196°C) were added into tube and the tube was sealed under high vacuum. The tube was allowed to stand at -15 °C for 2 days to prepare DCA-VCM adducts.

#### *Polymerization of the DCA-monomer Adduct*

The tube which contains DCA-monomer adduct was  $\gamma$ -ray irradiate (dose rate 2 Mrad/h) for 1 hour at -78 °C to initiate polymerization. Postpolymerization was carried out at -15 °C for 4 days.

#### *Separation of Polymer after Postpolymerization*

After postpolymerization, the DCA-polymer adduct was poured into the excess methanol. The precipitated polymer was filtered off and washed with absolute methanol repeatedly, and dried under vacuum.

#### **Measurements**

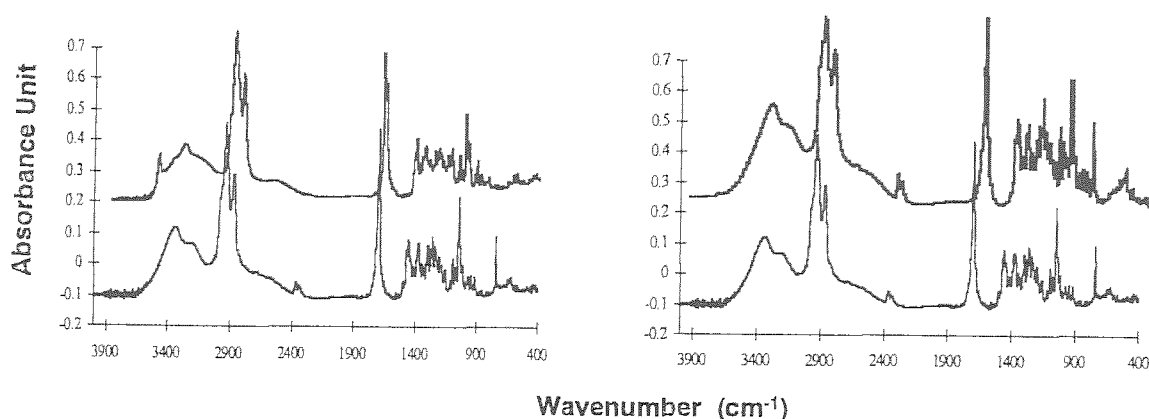
Infrared Spectrum of DCA-solvent adduct, guest free DCA, DCA-monomer adduct, DCA-polymer adduct and obtained polymer were measured with Bruker Equinox55/S spectrometer by using KBr pellet technique. DSC measurements were made for determining guest-releasing point, melting point of crystal and Tg of obtained polymer on Nertzsch DSC 200 at scan rate 10°C/min and scan range of 25-200°C under nitrogen atmosphere. TGA/DTA measurements were made for determining thermal stability of guest in DCA host and thermal stability of the obtained polymer on Rigaku Thermoplus. Thermogravimetric and Differential Thermal Analyzer at scan rate 10

K/min under nitrogen atmosphere. Powder X-ray diffraction studies were performed by using the horizontal X-ray diffractometer D/MAX-2000 analyzing at room temperature at angle range ( $2\theta$ ) 3-25°.

## RESULTS AND DISCUSSION

### *Properties of DCA Inclusion Compound with various solvents*

The inclusion compounds of DCA with various solvents are usually prepared by a recrystallization method. In the case of DCA, the spectrum shows the O-H stretching



**Figure 2.** FTIR of; DCA powder (left, top), DCA with *o*-xylene guest (left, below and right, below), and DCA with dioxane guest molecules (right, top).

band around 3500-3000  $\text{cm}^{-1}$ , free-hydroxy peak around 3500  $\text{cm}^{-1}$ , and carbonyl doublet peak at 1714 and 1699  $\text{cm}^{-1}$ . As shown in Figure 2, the free hydroxy peak of DCA disappeared after forming inclusion compound with *o*-xylene. The carbonyl doublet of DCA changes to a peak and shifts to lower wavenumber around 1690  $\text{cm}^{-1}$ . Furthermore, the C-H out of plane vibration of *o*-xylene at 739  $\text{cm}^{-1}$  is significant when DCA forms inclusion compound with *o*-xylene. This indicates that DCA molecules form hydrogen-bonding networks in the molecular assemblies. In the case of dioxane, and *p*-xylene, similar results are observed. It is found that ethyl acetate can be entrapped in the DCA channel as observed from the carbonyl peak of acetate at 1742  $\text{cm}^{-1}$ .

Thermal stability of guest molecules in DCA channel and molar ratio of compounds was determined by TG/DTA. Figure 3 shows DTA and TG thermograms of the DCA intercalating with dioxane. The peak at lower temperature corresponds to the temperature at which the solvent guest is released from DCA crystals.

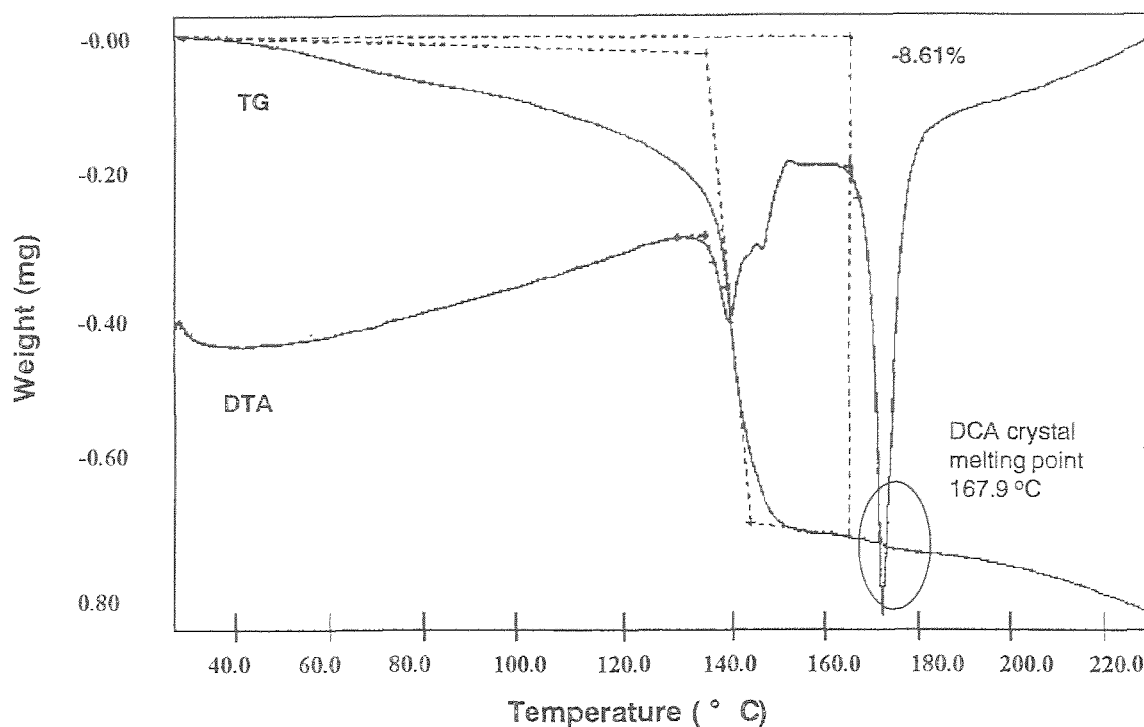


Figure 3. Thermal stability of DCA with dioxane as a guest molecule.

The weight loss of the guest peaks at 136-154°C can be calculated as a molar ratio of host and guest. The molar ratio between host and guest and guest releasing point are summarized in Table 1.

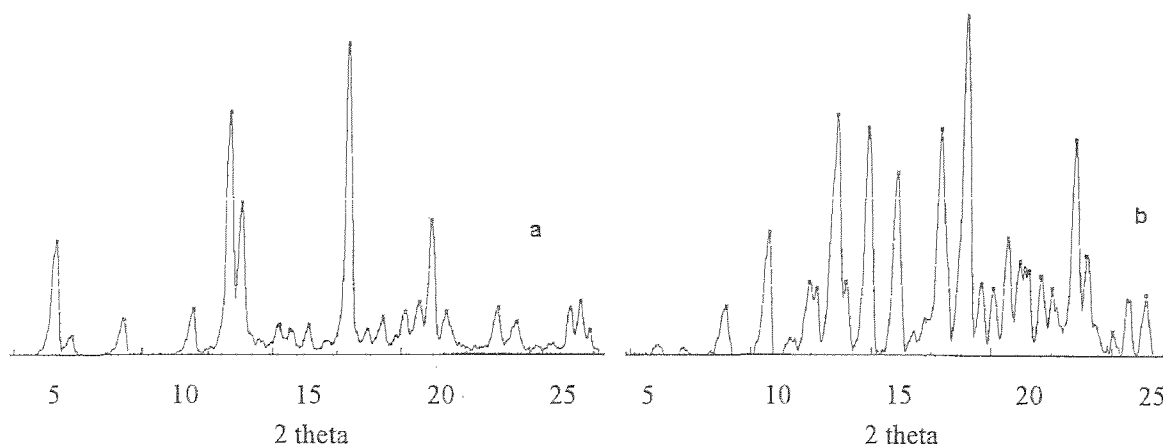
As shown in Table 1, the molar ratios of host/guest for *o*-xylene and *p*-xylene are about two indicating that two DCA molecules include one molecule of guest. The ratio of ethyl acetate is much higher than others may be regarded as a result of the guest disorder in the host channel.

The unique feature of DCA in the inclusion compound application is the stability of guest free DCA crystal. Hence, a host guest compound can be prepared by a guest absorption or intercalation method, which is very useful for the guest that can not be

directly recrystallized with DCA. Firstly, the completion of guest removal was confirmed by FTIR, followed by XRD and TGA.

**Table 1.** Thermal stability and molar ratio of DCA inclusion compound in various solvents as guest

Guest	Guest releasing point (°C)	Percentage of weight loss	Molar ratio of DCA/guest
dioxane	143.2	8.61	2.38
Ethyl acetate	150.4	3.74	5.77
<i>o</i> -xylene	152.1	11.62	2.05
<i>p</i> -xylene	153.9	11.64	2.05



**Figure 4.** XRD patterns of; a) DCA with *o*-xylene guest and b) after guest removal.

XRD studies also support that the removal of guest *o*-xylene from DCA-*o*-xylene is successful as shown in Figure 4. Here, after guest removal, the XRD pattern of DCA turns back to be as an original DCA powder.

As shown in Figure 5, when the guest molecules are completely excluded, TG/DTA shows only the  $T_m$  of DCA.

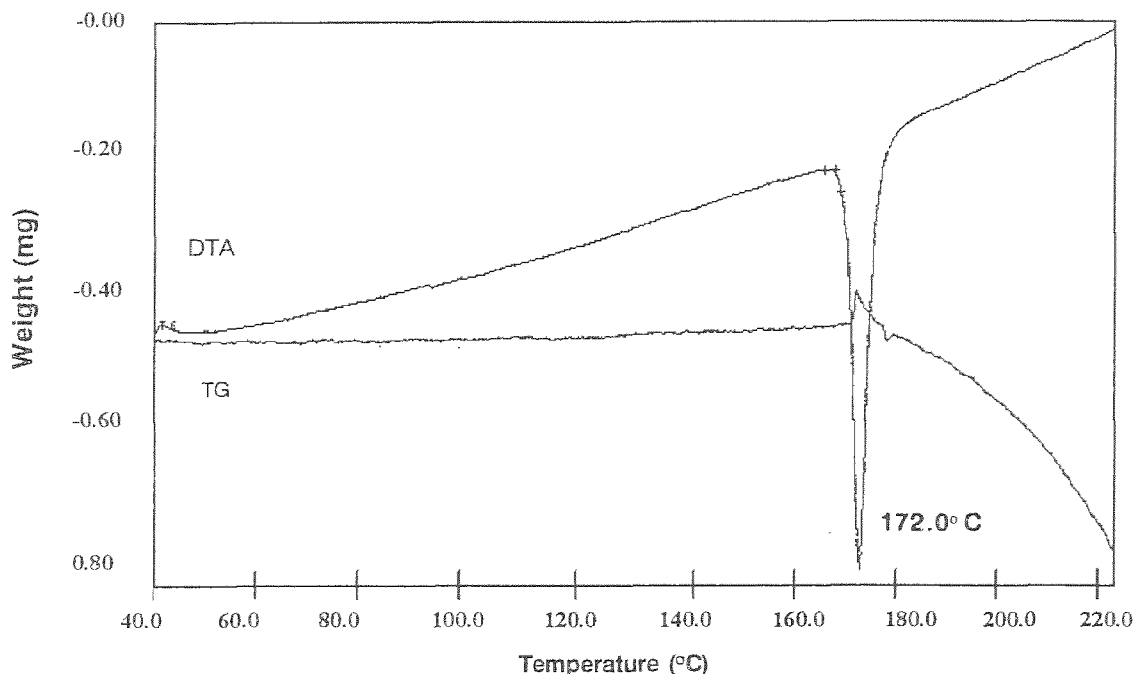


Figure 5. Thermogravimetry of DCA after completion of guest removal.

*Properties of DCA-VCM, DCA-VCM inclusion polymerization and DCA-PVC adduct*

Owing to the instability of VCM, it is difficult to assure that VCM will be stabilized in DCA as a guest compound. Here, trichloroethylene was used as a model compound to confirm the stability of this compound in DCA channel.

As shown in Figure 6, the FTIR of the obtained compound can be concluded that trichloroethylene is entrapped as a guest.

XRD pattern also shows the changing of DCA structure as a result of guest entrapment (Figure 7) by intercalation process.

Thermal analysis also indicates that there is trichloroethylene guest as observed from the guest releasing diagram (Figure 8).

An attempt to study the inclusion of VCM in DCA was done by using DSC. As shown in Figure 9, vinyl chloride monomer releasing temperature was observed at around 48°C.

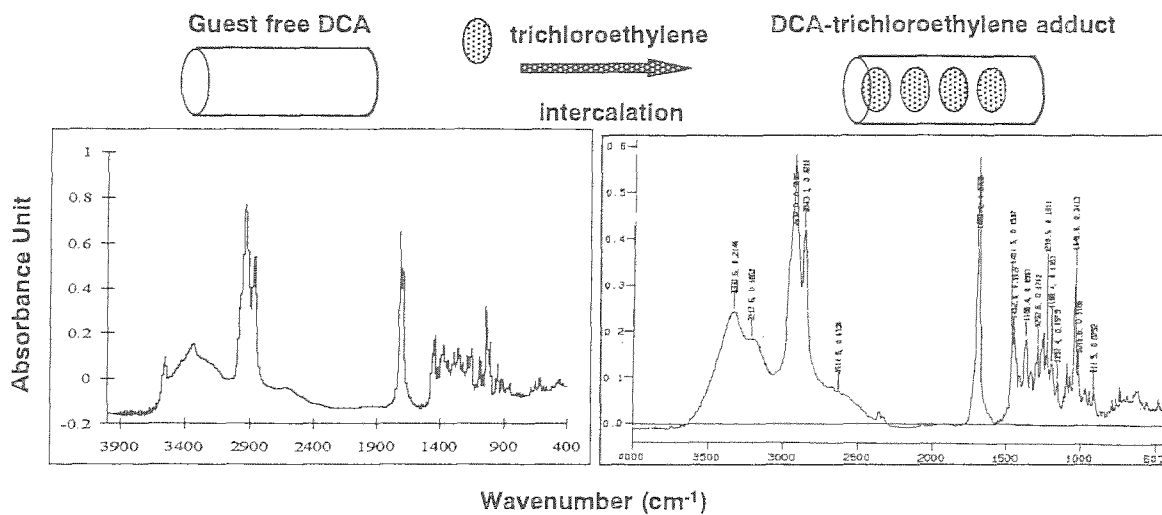


Figure 6. FTIR of DCA with trichloroethylene molecule

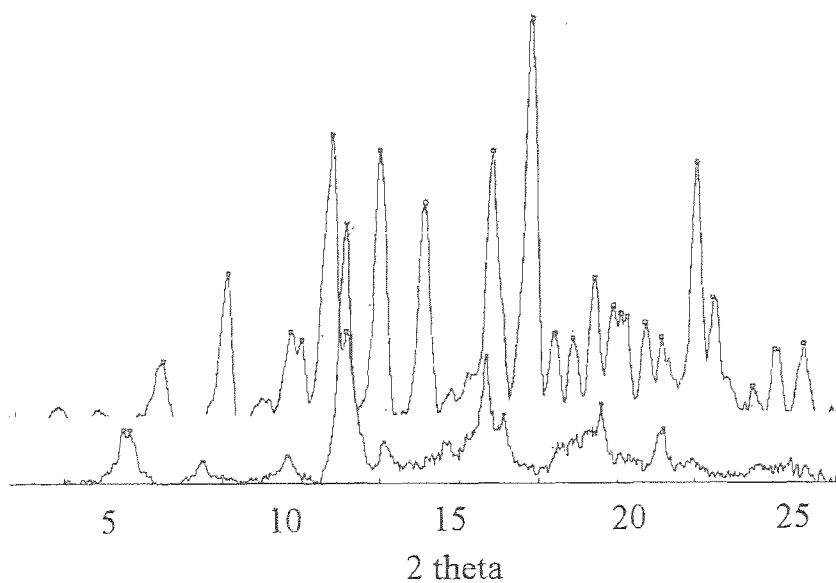


Figure 7. XRD pattern of DCA (back) and after intercalation process by absorption of trichloroethylene for 2 days (front).

DCA-VCM crystal was allowed irradiation by  $\gamma$ -ray at various dose rates to confirm that the polymerization process. It is found that the dose rate at 1 Mrad or 2 Mrad gives similar molecular weight and yield percent of the obtained product at approximately 2000 as referred to polystyrene by using GPC technique. Here, 2 Mrad



was chosen as a procedure to study whether the obtained compound is PVC and the successful of the controlled structure.

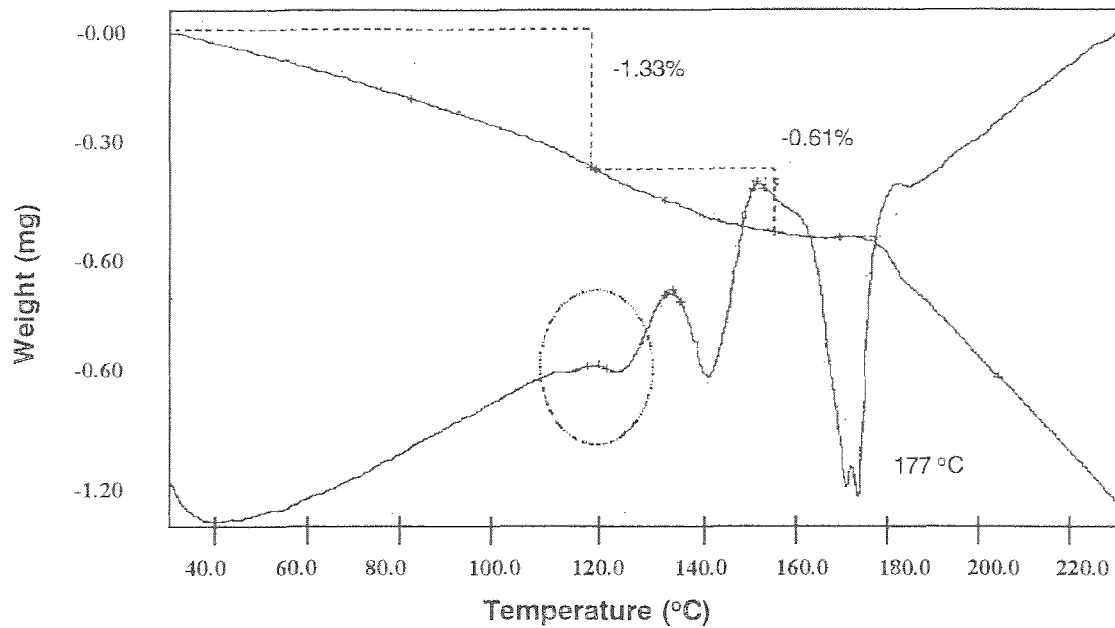


Figure 8. TGA of DCA after intercalation process with trichloroethylene.

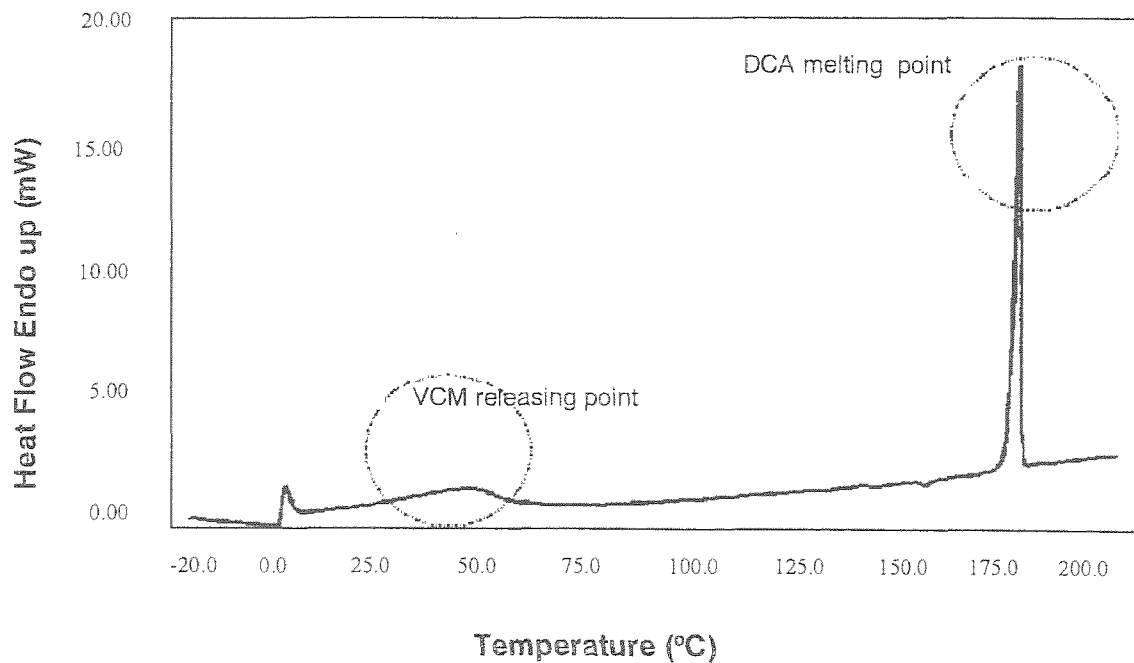


Figure 9. DSC of DCA after intercalation process with VCM.

Thermal stability study on the DCA-PVC adduct indicates the releasing point of the PVC from the host to be at 100-120 °C (Figure 10). In other words, DCA-VCM intercalation is found to be successful.

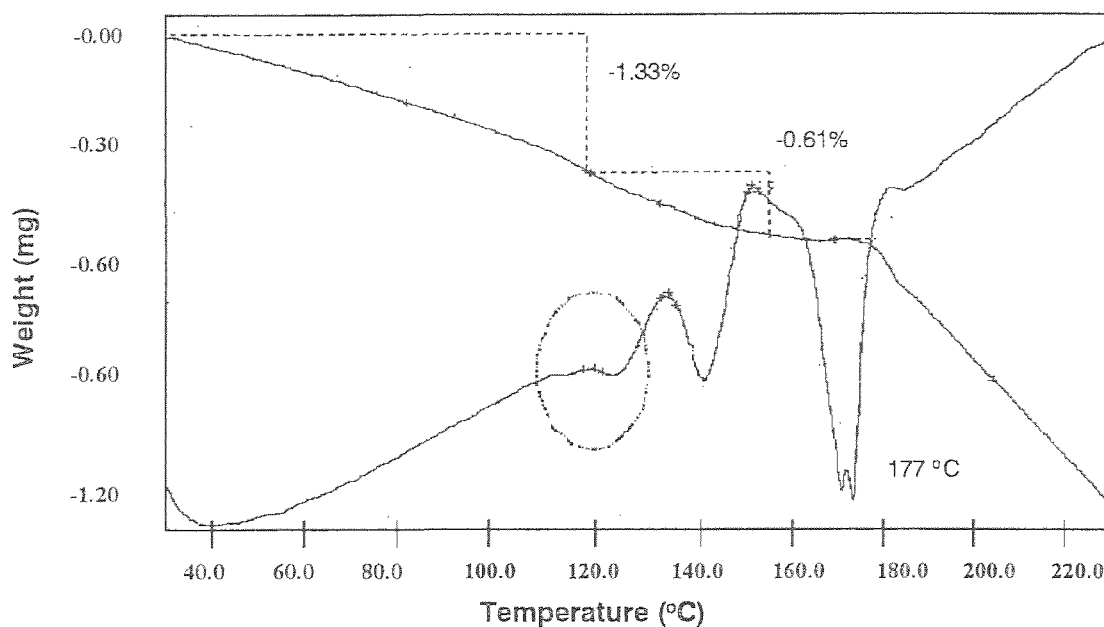
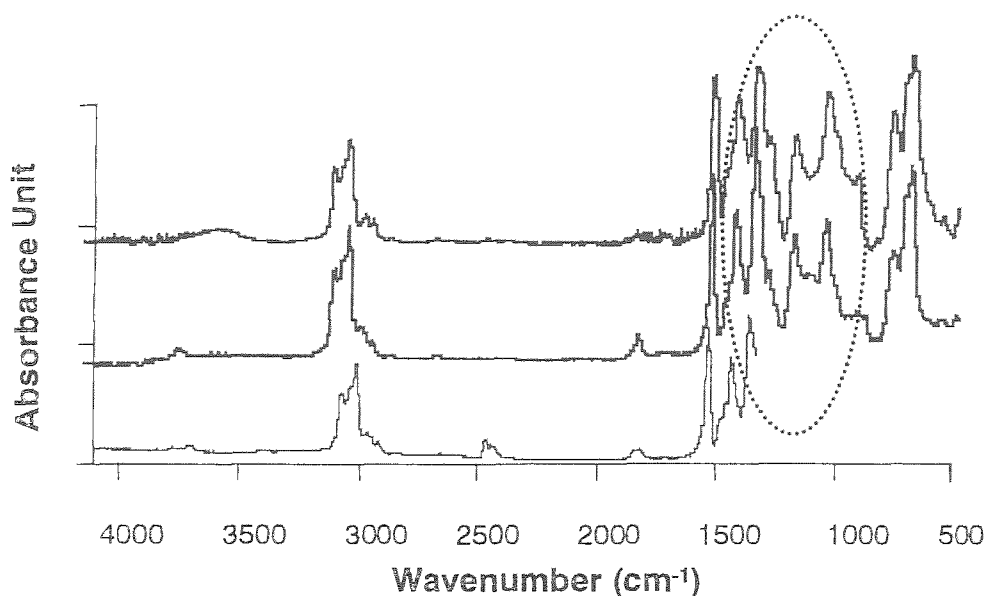


Figure 10. TGA of DCA-VCM after  $\gamma$ -ray irradiation for 20 Kgy.

#### *Study on microstructure of resulting polymers*

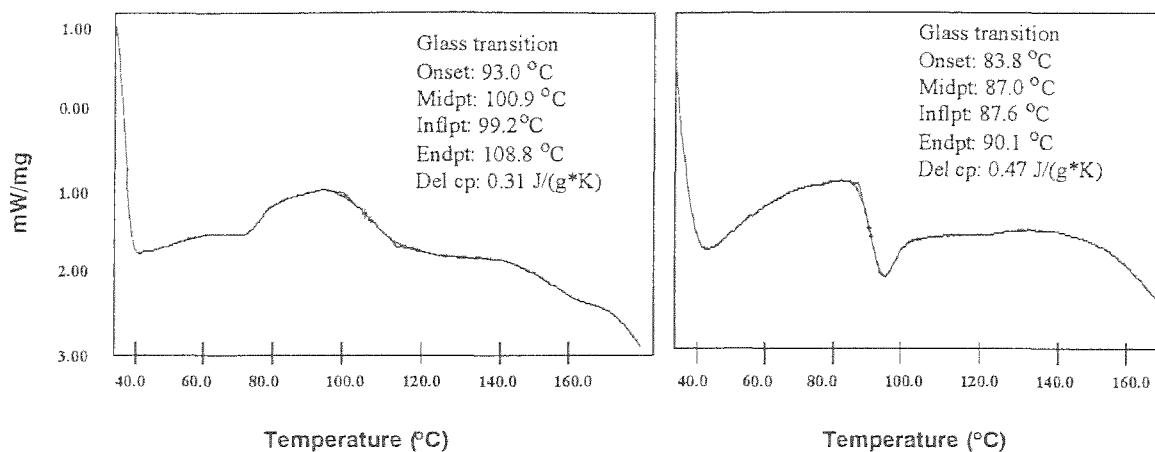
Figure 11 shows the obtained products from inclusion polymerization, which DCA-VCM were prepared from two types of guest free DCA, i.e. guest free DCA from DCA-dioxane and guest free DCA from DCA-ethyl acetate. Comparing the FTIR spectrum of the PVC obtained by the inclusion polymerization with the commercial poly(vinyl chloride), the resulting polymer can be concluded as a poly(vinyl chloride). It should be noted that there are some differences of these spectra, especially in the band around  $1250\text{ cm}^{-1}$ , which is assigned to the vibration mode of methine (CH). The PVC from the inclusion polymerization shows two sharp bands at  $1257\text{ cm}^{-1}$  and  $1228\text{ cm}^{-1}$  while the commercial PVC shows the methine (CH) band at  $1250\text{ cm}^{-1}$ . This indicates that the resulting polymer may have specific structure owing to the higher regularity than the commercial PVC.



**Figure 11.** FT-IR of commercial PVC (top), inclusion PVC obtained from DCA-dioxane guest free system (middle), and inclusion PVC obtained from DCA-*o*-xylene guest free system (bottom).

Another information from FT-IR and FT-NMR (see next section) is that, the obtained polymers prepared from different guest free DCA compounds give the similar structure. These results also indicate that the provided channels studied in this work are structurally similar in shape and size.

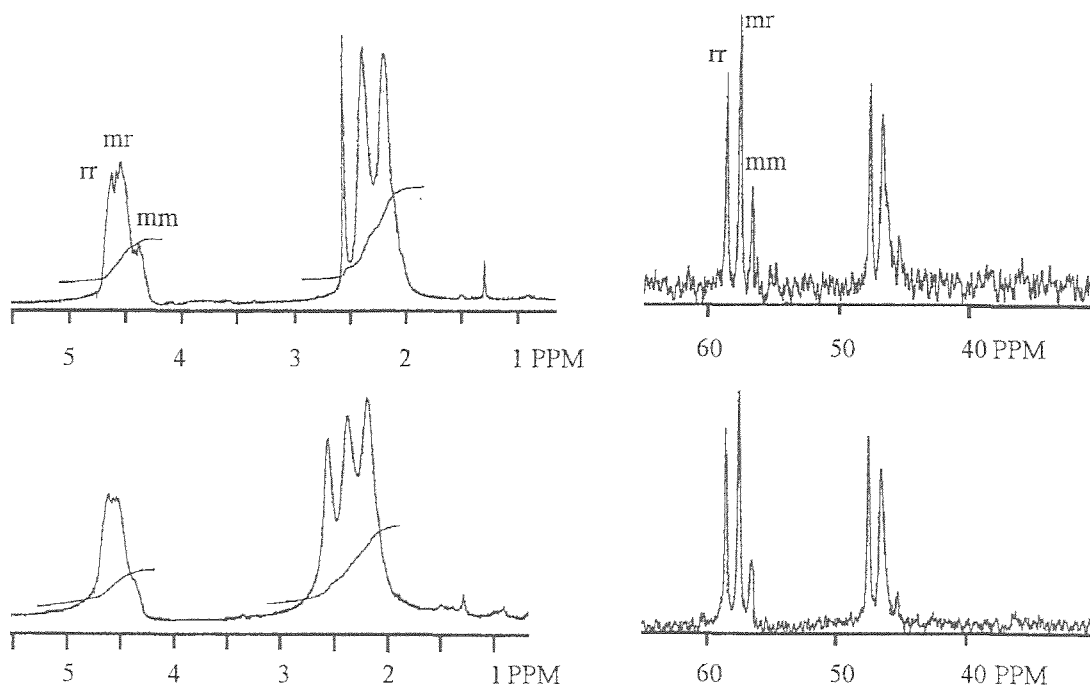
Thermal stability study by DSC (Figure 12) shows that the glass transition temperature ( $T_g$ ) of the obtained PVC is slightly higher than the commercial PVC. However, in the case of the obtained PVC, the range of  $T_g$  peak is broader than the commercial PVC, which may due to the broad distribution of the regularity in the product.



**Figure 12.** Thermal property of the commercial PVC and the obtained PVC as observed by DSC.

*NMR study on the obtained PVC and the commercial PVC*

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicate that there are differences in the structure between the commercial PVC and the obtained PVC. It is found that the ratio between mm, mr, and rr are drastically changed in both spectrum (Figure 13).



**Figure 13.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of the commercial PVC and the obtained PVC.

Although it has been expected that with the specific alignment of VCM in the channel of DCA, the obtained product should be an isotactic rich product. Here, it is clearly that the obtained PVC is rather syndiotactic rich which might have been a result from the channel structure of DCA. For example, it can be thought that the zigzag channel of DCA will make most of VCM aligned in an alternative way to make the polymer be a syndiotactic rich polymer. Although, there are many factors that can be considered in the tacticity of the inclusion polymerization, at the moment, we are focusing on the post polymerization temperature and time.

### Conclusion

DCA is found to be a useful host compound owing to two main reasons. The first is DCA can be prepared as a solvent free or guest free DCA crystal. The second is the intercalation process produces the DCA with another guest molecule, which in this case the vinyl chloride monomer. Radical polymerization by  $\gamma$ -ray irradiation is proven to generate polyvinyl chloride monomer with a syndiotactic rich structure.

### Acknowledgment

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### References:

1. Takemoto K; Sonoda N. In *Inclusion Compound 2*; Academic Press: London, 1984; pp 47-67.
2. Matsumoto, A.; Matsumura, T.; Aoki, S. *Macromolecules*. 1996, 29, 423-432
3. Miyata, M.; Noma, F.; Okanishi, K. *J. Inclusion Phenom.* 1987, 5, 249-252.

## 21. Conclusion Remarks for Takasaki Workshop on Bilateral Cooperations

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The main theme in this workshop was the radiation processing to natural polymers, which are abundant and familiar to our life materials in Asian countries. For past fourth decades, the radiation processing had been focused to synthetic polymers as plastics and rubbers. It has been well recognized that the cross-linking is the most useful radiation reaction for processing of polymer modification, that is, the improvement of polymer properties such as mechanical strength, heat resistance, forming, adhesive, memory effect, etc. The characteristic of radiation could be defined that the chemical reactions can be induced at lower temperature with the uniform distribution in polymer matrix, and the reactions can control easily. Therefore, the shape or structure of materials could be well maintained by radiation processing even if the materials are small particles or thin films.

All of the natural polymers as chitin and chitosan, silk fibers, and marine carbohydrate are intrinsically functional materials, and they have a sophisticated structure. The specific characteristics of radiation effects would be profitable for the processing of natural polymers, because the radiation effects may occur selectively in the materials, that is, a specific part of the materials is preferentially changed and major part is remained.

The presentation in this workshop showed many interesting and fruitful results, namely, the hydrogel may be produced from starch by radiation, a wound dressing is made from Chitin, and a coating agent for fruit preservation can be obtained from sea plants by radiation. These results indicate a new trend in radiation processing. The modification of natural polymers should be an important processing in 21-century.

# 国際単位系 (SI) と換算表

表1 SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表3 固有の名称をもつSI相立単位

量	名称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	s <sup>-1</sup>
力	ニュートン	N	m·kg·s <sup>-2</sup>
圧力、応力	パスカル	Pa	N·m <sup>-2</sup>
エネルギー、仕事、熱量	ジュール	J	N·m
仕事、放射束	ワット	W	J·s <sup>-1</sup>
電気量、電荷	クーロント	C	A·s
電位、電圧、起電力	ボルト	V	W·A <sup>-1</sup>
静電容量	ファラド	F	C·V <sup>-1</sup>
電気抵抗	オーム	Ω	V·A <sup>-1</sup>
コンダクタンス	ジーメン	S	A·V <sup>-1</sup>
磁束	ウェーバ	Wb	V·s
磁束密度	テスラ	T	Wb·m <sup>-2</sup>
インダクタンス	ヘンリー	H	Wb·A <sup>-1</sup>
セルシウス温度	セルシウス度	°C	
光度	ルーメン	lm	cd·sr
照射度	ルクス	lx	lm·m <sup>-2</sup>
放射能	ベクレル	Bq	s <sup>-1</sup>
吸収線量	グレイ	Gy	J·kg <sup>-1</sup>
線量等量	シーベルト	Sv	J·kg <sup>-1</sup>

表2 SIと併用される単位

名称	記号
分、時、日	min, h, d
度、分、秒	°, ', "
リットル	L, l
トン	t
電子ボルト	eV
原子質量単位	u

1 eV = 1.60218 × 10<sup>-19</sup> J

1 u = 1.66054 × 10<sup>-27</sup> kg

表4 SIと共に暫定的に維持される単位

名称	記号
オングストローム	Å
バー	h
バル	bar
ガリ	Gal
キュリー	Ci
レントゲン	R
ラド	rad
レム	rem

1 Å = 0.1 nm = 10<sup>-10</sup> m

1 h = 100 fm = 10<sup>-8</sup> m

1 bar = 0.1 MPa = 10<sup>5</sup> Pa

1 Gal = 1 cm s<sup>-2</sup> = 10<sup>-2</sup> m s<sup>-2</sup>

1 Ci = 3.7 × 10<sup>10</sup> Bq

1 R = 2.58 × 10<sup>-4</sup> C kg<sup>-1</sup>

1 rad = 1e Gy = 10<sup>-2</sup> Gy

1 rem = 1e Sv = 10<sup>-2</sup> Sv

表5 SI接頭語

倍数	接頭語	記号
10 <sup>18</sup>	エクサ	E
10 <sup>15</sup>	ペタ	P
10 <sup>12</sup>	テラ	T
10 <sup>9</sup>	ギガ	G
10 <sup>6</sup>	メガ	M
10 <sup>3</sup>	キロ	k
10 <sup>2</sup>	ヘクト	h
10 <sup>1</sup>	デシ	d
10 <sup>0</sup>	センチ	c
10 <sup>-1</sup>	ミリ	m
10 <sup>-2</sup>	マイクロ	μ
10 <sup>-3</sup>	ナノ	n
10 <sup>-6</sup>	ピコ	p
10 <sup>-9</sup>	フェムト	f
10 <sup>-12</sup>	アト	a

(注)

- 表1-5は「国際単位系」第5版、国際度量衡局1985年刊行による。ただし、1 eVおよび1 uの値はCODATAの1986年推奨値による。
- 表4には海里、ノット、アール、ヘクターも含まれているが日常の単位なのでここでは省略した。
- barは、JISでは流体の圧力を表す場合に限り表2のカテゴリに分類されている。
- EC関係理事会指令では bar, barnおよび「血圧」の単位、mmHgを表2のカテゴリに入れている。

## 換算表

力	N (=10 <sup>5</sup> dyn)	kgf	lbf
1	1	0.101972	0.224809
9.80665	1	1	2.20462
4.44822	0.453592	1	1

密度 1 Pa·s (N·s·m<sup>-2</sup>) = 10 P (ポアズ) (g·cm<sup>-1</sup>·s)

動粘度 1 m<sup>2</sup>·s<sup>-1</sup> = 10<sup>6</sup> St (ストークス) (cm<sup>2</sup>·s<sup>-1</sup>)

力	MPa (=10 bar)	kgf·cm <sup>-2</sup>	atm	mmHg (Torr)	lbf in <sup>-2</sup> (psi)
1	1	10.1972	9.86923	7.50062 × 10 <sup>2</sup>	145.038
0.0980665	1	0.967841	735.559	14.2233	
0.103325	1.03323	1	760	14.6959	
1.33322 × 10 <sup>-3</sup>	1.35951 × 10 <sup>-3</sup>	1.31579 × 10 <sup>-3</sup>	1	1.93368 × 10 <sup>-2</sup>	
6.89476 × 10 <sup>-3</sup>	7.03070 × 10 <sup>-3</sup>	6.80460 × 10 <sup>-3</sup>	51.7149	1	

エネルギー・仕事・熱量	J (=10 <sup>7</sup> erg)	kgf·m	kW·h	cal (計量法)	Btu	ft·lbf	eV
1	1	0.101972	2.77778 × 10 <sup>-4</sup>	0.238889	9.47813 × 10 <sup>-4</sup>	0.737562	6.24150 × 10 <sup>18</sup>
9.80665	1	1	2.72407 × 10 <sup>-4</sup>	2.34270	9.29487 × 10 <sup>-4</sup>	7.23301	6.12082 × 10 <sup>18</sup>
3.6 × 10 <sup>3</sup>	3.67098 × 10 <sup>3</sup>	1	1	8.59999 × 10 <sup>3</sup>	3412.13	2.65522 × 10 <sup>3</sup>	2.24694 × 10 <sup>25</sup>
4.18605	0.426858	1.16279 × 10 <sup>3</sup>	1	1	3.96759 × 10 <sup>3</sup>	3.08747	2.61272 × 10 <sup>16</sup>
1055.06	107.586	2.93072 × 10 <sup>4</sup>	1	252.042	1	778.172	6.58515 × 10 <sup>21</sup>
1.35582	0.138255	3.76616 × 10 <sup>3</sup>	0.323890	1.28506 × 10 <sup>3</sup>	1	1	8.46223 × 10 <sup>16</sup>
1.60218 × 10 <sup>19</sup>	1.63377 × 10 <sup>19</sup>	4.45050 × 10 <sup>17</sup>	3.82743 × 10 <sup>17</sup>	1.51837 × 10 <sup>17</sup>	1.18171 × 10 <sup>17</sup>	1	1

1 cal = 4.18605 J (計量法)

= 4.184 J (熱化学)

= 4.1855 J (15°C)

= 4.1868 J (国際蒸気表)

仕事率 1 PS (馬力)

= 75 kgf·m/s

= 735.499 W

放射能	Bq	Ci
1	1	2.70270 × 10 <sup>-11</sup>
3.7 × 10 <sup>10</sup>	1	1

吸収線量	Gy	rad
1	1	100
0.01	1	1

照射線量	C/kg	R
1	1	3876
2.58 × 10 <sup>-4</sup>	1	1

線量当量	Sv	rem
1	1	100
0.01	1	1

(86年12月26日現在)

